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Ca chemisorption on Cu(100) in the submonolayer regime: Metastable and stable adsorption phases

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Ca adsorption on Cu(100) has been studied by high-resolution electron energy-loss spectroscopy, work-function measurements, and low-energy electron diffraction as a function of coverage, up to one monolayer, at 110 and 300 K. At each coverage a condensed phase is formed at 110 K that irreversibly transforms into a dispersed phase upon heating. The 300-K data suggest that Ca occupies substitutional sites at this temperature. A comparison with the chemisorption of alkali metals is presented.

In many respects the properties of alkaline-earth metal adsorbates such as Ca, Sr, and Ba on metal surfaces are expected to be similar to those of the alkali metals (AM). For example, the calculated dipole moment induced by Ca and Sr grows linearly with distance from the substrate as for AM and the charge density induced by the light alkaline-earth metals closely resembles that of AM adatoms.[1] In agreement with this picture, it has been found that for Ba on Cu(111) the measured coverage dependence of the change in work function and of the valence-band photoemission spectra up to a coverage of one monolayer matches that of AM adsorbates and consequently has been interpreted in terms of charge transfer from Ba adatoms to the substrate at low coverages.[2] On the other hand *d* states, which are unoccupied on the free atoms, are partially filled in the chemisorbed or metallic state and therefore Ca, Sr, and Ba could behave in some aspects similarly to the neighboring transition metals.[1,3] However, mainly the electronic properties of thick films have been investigated until now and no vibrational spectra have been reported.

If chemisorbed Ca behaves like an AM atom, a large charge redistribution is expected on going from very low coverages to one monolayer.[4] Such a transition should significantly affect the high-resolution electron energy-loss (HREEL) spectra in agreement with what has been reported for alkalis metals on Cu.[5–8] In this work we present a combined HREELS, low-energy electron diffraction (LEED), and work-function study of Ca on Cu(100) as a function of coverage up to one monolayer. It is found that the coverage dependences of both the static and the dynamical dipole moment of adsorbed Ca closely follow those of AM atoms. However, in contrast to the AM atom case, no dispersed phase is observed at low temperature testifying to a stronger adatom-adatom attraction, probably related to the *d* orbital bonding. The 300-K data suggest that a substrate reconstruction has occurred at this temperature leading to a thermodynamically stable phase in which Ca substitutes for first-layer Cu atoms. The HREELS measurements were performed using an ELS22 spectrometer with the energy resolution set to 4–5 meV. The primary electron energy was 2.5 eV and the angle of incidence of the electrons was 60°. The spectra have been collected in the specular geometry at a working pressure of 2×10^{-11} mbar. After Ca evaporation the sample has been biased in order to correct for the change in work function.

The cleaning procedure, sample characterization, and Ca dosage have been carried out in a separate interconnected chamber (base pressure 6×10^{-11} mbar). The Cu(100) sample was cleaned by Ne^+ sputtering and annealing at 900 K until no contaminants could be detected by Auger electron and HREEL spectroscopies and the surface showed sharp LEED spots. Ca was sublimated from a small ingot of 98.8% purity placed in a W basket. During the evaporation the pressure rose to $1-2\times10^{-10}$ mbar due to H_2 degassing from the Ca source.

Immediately after the dosage at 300 K (RT) no contaminant peaks could be detected either by HREEL or by Auger spectroscopies. Approximately 40 min after the evaporation an oxygen feature becomes visible in the HREEL spectra at about 44 meV and reaches an intensity of 1×10^{-4} that of the elastic peak in about 1.5 h. The appearance of the oxygen loss influences neither the frequency nor the intensity of the Ca feature. When Ca was evaporated at 110 K we always observed that the 44-meV and H related features were visible in the 100-meV region. The intensity of these losses was lower than 3×10^{-4} and 2×10^{-4} that of the elastic peak, respectively. All HREELS data reported here have been normalized to the elastic peak.

The coverage (θ) has been determined from the measurement of the ratio (R) of the Ca 294- and Cu 920-eV Auger peaks in the first derivative mode. The plot of R versus evaporation time is composed of linear segments and the first kink in this plot was associated with the completion of the first Ca monolayer (ML). The shape of the Ca 294-eV peak of the sample dosed and measured at 110 K is different from that of the sample at 300 K. Therefore the R versus evaporation time curve has been measured at both temperatures. If the sample dosed at 110 K is heated to RT the Ca 295-eV peak irreversibly assumes the characteristic shape of the 300-K phase. Due to the different shape R is lower at 110 K than at 300 K for each coverage by about a factor 0.8. Since we obtained the same value of R by heating to RT one Ca

ML dosed at 110 K or by evaporating one ML at RT, the Ca density, at the saturation of the first ML, is the same at both temperatures. We can therefore determine the number of Ca atoms per Cu first-layer atom at the completion of the first ML from the LEED pattern at 110 K (see the discussion below). It amounts to 0.45 ± 0.04. In the following we assign this ratio to $\theta=1$. For each coverage the work function has been measured by the diode method.

Figure 1 shows the coverage dependence of the work-function change, $\Delta\phi$, for samples dosed and measured at 300 K (dots). The general behavior of the $\Delta\phi$ vs θ curve of Ca at submonolayer coverages is very similar to that of AM chemisorbed on metals showing a rapid decrease with a minimum at about half the saturation coverage, followed by an increase, which saturates at the completion of the first ML. $\Delta\phi$ at the minimum amounts to -1.8 eV, while the saturation $\Delta\phi$ for the complete ML is -1.7 eV. The latter $\Delta\phi$ corresponds to an absolute value of the work function of 2.9 eV which is very close to that of metallic Ca (2.87 eV) (Ref. 9) and slightly smaller than the theoretical value for the saturated ML (3.13 eV).[3] From the $\Delta\phi$ vs θ plot, using the method described in Ref. 10 and assuming that the Ca-Ca distance decreases as $\theta^{1/2}$, a polarizability (α) of 2.1×10^{-23} cm^3 is obtained which is of the same order of magnitude as the polarizability of atomic Ca ($\alpha=2.3\times10^{-23}$ cm^3).[11]

In Fig. 2 we present the Ca/Cu(100) HREELS spectra measured at 300 K after dosing at the same temperature. After Ca deposition a peak appears in the spectrum at 16.5 ± 0.5 meV, which can be straightforwardly attributed to the dipole-active Ca-Cu stretching mode.

For each coverage the energy and the intensity of this loss feature have been determined by a least-squares Gaussian fit of the spectrum and the intensity is plotted in Fig. 3 (dots). No coverage dependence of the energy loss is observed within our experimental error (±0.5 meV) while the intensity increases linearly up to about $\frac{1}{5}$ of the saturation coverage and then rapidly decreases. This behavior is very similar to what has been observed for AM on Cu.[5–8] The coverage dependence of the intensity of the stretching mode, calculated taking into account the dipole-dipole interaction[12] and assuming the Ca-Ca distance to be proportional to $\theta^{-1/2}$, is also shown in Fig. 3 (continuous and dashed lines). The continuous line has been obtained using the polarizability value deduced from the work-function change measurements and a constant value of the effective charge q^* equal to $0.8e$, where e is the electronic charge. As in the case of alkali metals on Cu (Refs. 5, 6, and 8) the coverage dependence of the intensity cannot be well fitted by assuming a constant q^*. A better fit is obtained by assuming that q^* decreases linearly to 50% of its initial value on going from the single adsorbed atom to saturation coverage (dashed line). The same assumption was used in Ref. 6 for the

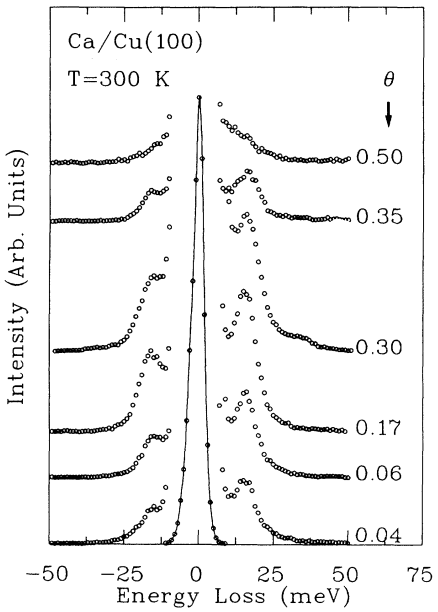

FIG. 2. Coverage evolution of the HREEL spectra of Ca/Cu(110) at $T=300$ K. The scaling factor is 50 for all spectra.

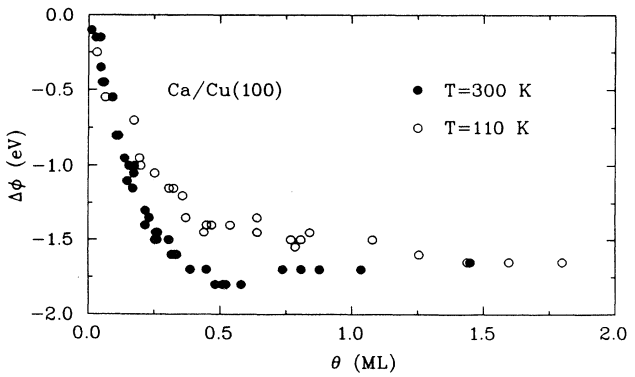

FIG. 1. Coverage dependence of the work-function change for Ca/Cu(100) at $T=300$ K (dots) and $T=110$ K (open circles).

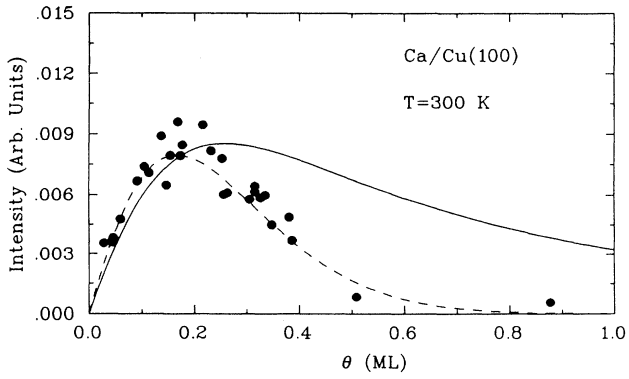

FIG. 3. Intensity of the Ca-Cu stretching mode as a function of coverage (dots) at $T=300$ K. The continuous and dashed lines show the calculated dependence of the intensity taking into account the dipole-dipole interaction: for the continuous line a constant value of $q^*=0.8e$ is assumed in the calculation, while a coverage dependent q^* (initial value $q^*=1e$) is used for the dashed line (see text).

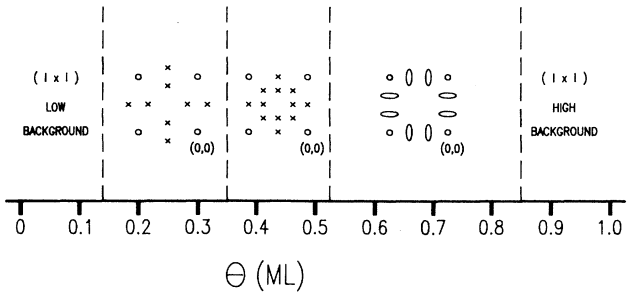

FIG. 4. LEED patterns observed in the different coverage ranges for the Ca/Cu(100) system at $T=300$ K. Open circles represent substrate spots.

AM/Cu case based on the fact that the calculated q^* value for a single chemisorbed AM atom[1,13] is about twice that calculated for the saturated ML.[14] The decrease of q^* reflects the charge redistribution which occurs upon increasing the coverage, when the adatoms come closer and direct Ca-Ca bonds are formed. The initial values of q^* compatible with our experimental data range from $0.8e$ to $1e$. These values are significantly higher than the ones that can be obtained for q^* from the plot of the calculated Ca-induced dipole moment of Ref. 1 ($q^*=0.22e$).

In Fig. 4 we sketch the LEED patterns that have been observed in the different coverage ranges for Ca dosed at 300 K. The adsorbate-induced diffraction spots were always weaker at RT than at low temperature and accompanied by a high background intensity indicating that a high degree of disorder is present in the overlayer structure. Moderate heating (520 K) and/or cooling to 110 K temperature did not improve the quality of the diffraction patterns. We have not been able to identify the real-space structures giving rise to these LEED patterns, but it seems that the size of the unit cell decreases as a function of coverage pointing to a reduction of the Ca-Ca distance with increasing θ in agreement with the analyses of the HREELS data.

Samples dosed at 110 K and annealed at 300 K show the same $\Delta\phi$, HREELS spectra, and LEED patterns. No changes are observed for samples dosed at 300 K and cooled at 110 K for the measurements.

Completely different results have been found instead by dosing Ca at 110 K and measuring at the same temperature. At 110 K the Ca stretching mode shows up in the HREELS spectra with an intensity lower than 1×10^{-3} at all coverages we have measured ($0.05\leq\theta\leq0.85$). This value is about a factor of 10 lower than that at the maximum of the intensity versus θ curve measured at 300 K. The energy of the Ca stretching mode at 110 K lies below 23 meV, but, because of its weakness, it is masked by the tail of the elastic peak and we cannot extract the exact value from our data. Since such a low value of the intensity is reached in the 300-K data only for coverages higher than 0.5 ML we deduce that at 110 K island formation occurs from the lowest coverages.

This interpretation is confirmed by the LEED pattern: for $\theta\geq0.05$ we observe 12 extra spots corresponding of two incommensurate hexagonal domains rotated by 15° from either the [001] or the [010] axis of the substrate, i.e., 90° one with respect to the other. The Ca-Ca nearest-neighbor distance obtained from the LEED pattern amounts to 4.1 ± 0.2 Å. Within this experimental uncertainty the Ca-Ca nearest-neighbor distance does not show any coverage dependence and is approximately that of metallic Ca (3.95 Å).

The different Ca overlayer structures obtained at high and at low temperatures are reflected also in the different behavior of the coverage dependence of $\Delta\phi$ (see Fig. 1). For coverages larger than $\frac{1}{6}$ of the saturated ML $\Delta\phi$ of the low-temperature phase (Fig. 1 open circles) is always smaller than the corresponding value for the 300-K phase, testifying to a smaller static dipole moment.

The overlayer geometry for an electropositive adsorbate is determined, in general, by a balance among the localization effects of the adsorbate-substrate potential, the screened electrostatic repulsion, and the attractive lateral interaction among adsorbates. In the case of AM at low coverages, the first two interaction terms dominate and therefore disperse phases are observed. At higher coverage the depolarization effect weakens the dipoles and the attractive term becomes dominant.[10,15] For K and Cs on graphite,[16,17] K/Cu(100),[18] and K/Ag(100) (Ref. 19) a two-dimensional condensation of the adsorbed AM atoms has been observed once a critical coverage θ_c, which ranges from $\frac{1}{3}$ to $\frac{1}{2}$ of a ML depending on the system, is reached. The value of θ_c for Ca/Cu(100) is significantly lower ($\theta_c\leq\frac{1}{20}$ ML), indicating that for this system the attractive term dominates even at the lowest coverages. Since theoretical calculations indicate that at least one electron occupies the $3d$ levels even for a single chemisorbed atom,[1] it is likely that the stronger attractive interaction arises from direct d bonding between adjacent Ca atoms.

While for the adsorbed AM mentioned above the condensed phase is thermodynamically stable,[16,19] for Ca/Cu(100) it evolves irreversibly into more open structures upon heating. The mobility of the Ca atoms being high also at 110 K, as testified by the existence of an ordered LEED pattern, the adlayer should reach the equilibrium configuration even at this low temperature. Since this is not the case, a mechanism which involves structural changes of the substrate must be invoked for the transition.

We suggest that Ca/Cu(100) behaves similarly to Na/Al(111). For this system at 140 K a condensed phase has been observed that transforms irreversibly into more open structures upon heating.[20,21] The low coverage high-temperature phase [$(\sqrt{3}\times\sqrt{3})R30°$], which is visible for θ up to about half a ML,[20] is related to a reconstruction of the substrate with Na atoms occupying substitutional sites formed by the removal of first-layer Al atoms,[22,23] while at higher coverages Na interdiffusion occurs.[24] One should note that for this system the difference in the coverage dependence of the work function (ϕ) at low and high temperatures[20] is similar to what we observe for Ca/Cu(100).

A reconstruction which involves Ca substitution of first-layer Cu atoms is not necessarily in disagreement

with the high dynamical dipole moment of the Ca-Cu stretching mode we observe at 300 K. In fact, if we assume a hard-sphere model, the Ca atom center would be about 0.9 Å above the top of the Cu surface atoms because of the difference in size of the Ca and the Cu atoms (3.95 and 2.55 Å, respectively). Therefore, the screening of the Ca dipole by the neighboring Cu atoms will not be very efficient. This situation is similar to that of the K-induced missing-row reconstruction on Cu(110) at low coverages where the K atom sits in a tiny trough created by the displacement of two or three Cu first-layer atoms[25] but conserves its strong dynamical dipole moment.[6] We can exclude, for coverages less than 1 ML, Ca interdiffusion below the Cu first-layer atoms on the basis of the behavior of R versus evaporation time (t). In fact (a) even at 300 K the R vs t plot is linear up to 1 ML, where it shows a kink; (b) the value of R at 300 K is for each θ about 20% higher than at 110 K while one would expect the opposite if interdiffusion had occurred and (c) at each θ the same value of R is obtained by dosing at 110 K and heating to RT or evaporating at RT.

In summary the work-function and HREELS data show that the coverage dependences of both the static and the dynamical dipole moment of adsorbed Ca strongly resemble those of adsorbed AM, testifying to a coverage-dependent charge redistribution that starts at very low θ (about $\frac{1}{5}$ of a ML). In contrast to the AM atom case, no dispersed phase is observed at low coverages at 110 K. This behavior is probably related to the stronger adatom-adatom attraction due to d orbital bonding. The 300-K data strongly suggest that a reconstruction has occurred at this temperature leading to a thermodynamically stable phase. This phase might involve Ca atoms substituting for first-layer Cu atoms.

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